

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in and relating to the preparation of Polyoxyalkylene Compounds

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for preparing polyoxyalkylene compounds and in particular for preparing such polyoxyalkylene compounds having a low "ash" content.

There are several well known methods for preparing polyoxyalkylene compounds and these methods generally comprise reacting, usually under pressure, an alkylene oxide such as ethylene oxide or 1:2, propylene oxide or a mixture of such alkylene oxides, in the presence of an alkaline catalyst with an organic compound containing a hydroxyl group such as a glycol or alcohol. The alkaline catalyst, which is usually an alkali metal or its hydroxide or its alkoxide is then treated with an acid, generally with an inorganic acid such as sulphuric acid or phosphoric acid. The inorganic salt which is formed during this acid treatment is then removed by decantation, filtration or centrifuging. Although such treatment will remove most of the inorganic salt some remains either dissolved or more generally finely dispersed in the polyoxyalkylene compound. This remaining salt may be present in proportions of up to 0.3% by weight. This remaining salt is known as "ash". This "ash" content may be determined by the Institute of Petroleum Standard Test Method 4/53 and in this Specification the term "ash content" is intended to mean "ash" content as determined by this method. Although such "ash" is not troublesome in many applications, it may give rise to serious problems in other applications, for

example when the polyoxyalkylene compound is used as a lubricant the inorganic salt may sediment out during use and the sediment may cause serious trouble. Furthermore polyoxyalkylene compounds having a low ash content have a decreased tendency to sludge formation and an increased heat stability. Even if the inorganic salt does not sediment out it may induce corrosion, for example polyoxyalkylene fluids having a high ash content are much more corrosive towards cadmium than ash free polyoxyalkylene fluids. This is particularly so if the salt is present as an acid salt.

It has now been discovered that polyoxyalkylene compounds having a very low ash content may be prepared by a process in which the alkaline catalyst is first removed by treatment with an acid and the reaction mixture then treated with a lower aliphatic alcohol or glycol and the suspended solid material removed.

Accordingly the present invention provides a process for preparing polyoxyalkylene compounds which comprises condensing an organic compound having at least one hydroxyl, carboxyl, mercapto, or primary or secondary amino group with one or more alkylene oxides in the presence of an alkaline catalyst, treating with a lower aliphatic alcohol or glycol and removing suspended solid material and the alcohol or glycol.

The organic compound containing at least one hydroxyl, carboxyl, mercapto or primary or secondary amino group which is starting material is usually a glycol, an alcohol, a mono-ether of a glycol or a phenol although other materials such as amino compounds for example butyl mono- or di-ethylamine or an N-methyl amide, carboxylic acids such as acetic acid, benzoic acid, toluic acid and abietic acid, mercaptans, for example dodecyl mercaptan

and especially branched chain mercaptans having from 6 to 18 carbon atoms per molecule may also be employed. The organic starting material may be prepared *in situ* in some cases, for example an organic amino compound to be used as starting material may be prepared *in situ* by the reaction between ammonia and an alkylene oxide such as for example propylene oxide. The glycol may be a low molecular weight glycol such as diethylene glycol or it may be a medium or high molecular weight polyoxyalkylene glycol which may have been prepared from the same alkylene oxide to be used in the present process or a different alkylene oxide or a mixture of alkylene oxides. Thus for example if the alkylene oxide to be used in the process is ethylene oxide the organic compound used as starting material may be a polypropylene glycol previously prepared by reacting propylene oxide with a lower propylene glycol. If a glycol is used as starting material it may be prepared *in situ* by the reaction between an alkylene oxide and water. Other polyhydric alcohols such as sorbitol and glycerol and partial ethers and esters thereof may be used. Organic compounds especially suitable as starting materials are monohydric alcohols. These alcohols may be primary, secondary or tertiary alcohols and their molecular weight is immaterial but low molecular weight alcohols such as those containing less than six carbon atoms per molecule for example secondary butanol, tertiary pentanol and especially n-butanol are preferred. High molecular weight alcohols, such as lauryl alcohol, may also be used. Other organic compounds containing hydroxyl groups which are preferred as starting materials are ethylene or propylene glycols or the dimers or trimers of such glycols or butylene glycol, and especially the monoethers of such glycols, particularly the mono-butyl ether of ethylene glycol. Also useful are alkyl phenols such as amyl and octyl phenols.

The alkaline catalyst used is preferably an alkali metal hydroxide for example sodium hydroxide, lithium hydroxide or preferably potassium hydroxide. The alkali metal itself, for example sodium or potassium may be used and this will of course generally react with the organic starting material, for example, if the latter is an alcohol an alkali metal alkoxide will be formed. Other substances which may be used as catalyst include quaternary ammonium bases such as trimethyl hydroxyethyl ammonium hydroxide.

The amount of catalyst required will vary according to its alkalinity, less being required if the catalyst is a strong alkali. However it is preferred that the amount of catalyst present should be between 0.15% and 1% by weight based on the total weight of reactants appearing in the final product.

All the alkaline catalyst may be present at the beginning of the reaction or it may be

added at definite stages throughout the reaction. In a process for preparing a polyoxyalkylene compound from a polyoxyalkylene compound of lower molecular weight it is preferred to add to the latter a solution of the alkaline catalyst in the lower molecular weight polyoxyalkylene compound or one having substantially the same molecular weight and to react the resultant solution with an alkylene oxide. This process may be repeated one or more times to give a product of the required molecular weight.

The alkylene oxide employed is preferably ethylene oxide, 1,2-propylene oxide or 1,2-butylene oxide although other alkylene oxides such as butadiene monoxide and amylene oxide may be used. Styrene and cyclohexene oxide may also be used and the term "alkylene oxide" is intended to include the cycloalkylene oxide and aryl substituted alkylene oxides.

Mixtures of alkylene oxides may also be employed, for example if a mixture of ethylene oxide and 1,2-propylene oxide is employed a polyoxyalkylene compound is formed in which the ethylene oxide and propylene oxide units are distributed randomly throughout the polyoxyalkylene compound in the same proportions as the alkylene oxides are present in the mixture used. Alternatively two different alkylene oxides may be used alternately or several different oxides may be used successively so giving block copolymers as described below.

The alkylene oxide or alkylene oxides used should preferably be pure and in particular should be substantially free from aldehyde and water. Alkylene oxides containing not more than 0.1% by weight of aldehyde and not more than 0.1% by weight of water are suitable for use in the process of the present invention.

When the required amount of alkylene oxide or alkylene oxides have reacted the reaction mixture is treated with an acid to neutralize the alkali catalyst. The term "to neutralize" is used to indicate that the added acid reacts with the alkali catalyst present and it is not intended to mean that the pH of the reaction mixture is brought to 7. Although in general it is preferable that the amount of acid added is just sufficient to react with all the alkali present, in other cases it may be desirable to add a slightly greater or a slightly small quantity of acid, preferred to use an inorganic acid but organic acids such as acetic acid may be employed. Most inorganic acids are suitable for this purpose. Thus phosphoric acid, sulphuric acid or hydrochloric acid may be used as weaker acids such as carbonic acid which may be introduced, for example, by blowing the reaction mixture with carbon dioxide. The amount of acid used should preferably be sufficient to react with all the alkaline catalyst present. Solid material forming during this neutralization step is preferably removed e.g., by filtration before the mixture is treated with

alcohol in the next step. However this solids removal may be omitted and all solids removed after the alcohol treatment step.

After the treatment with the acid a lower aliphatic alcohol or glycol is added to the reaction mixture. By lower aliphatic alcohol or glycol is meant an alcohol or glycol containing not more than 4 carbon atoms per molecule, thus suitable compounds are methanol, ethanol, propanol, butanol, ethylene glycol or propylene glycol but methanol is preferred.

The lower aliphatic alcohol or glycol to be added to the reaction mixture may be added for example in amounts between 3% and 100% by weight based on the weight of the reaction mixture and more preferably between 8% and 30% by weight. The alcohol or glycol and the reaction mixture should be thoroughly mixed, for example, by stirring. If the lower aliphatic alcohol is not completely miscible in all proportions with the reaction mixture it is preferred that the amount of lower aliphatic alcohol or glycol added is just sufficient to saturate the reaction mixture with the solvent. The correct amount of alcohol or glycol required for this purpose will vary according to the nature of the poly-oxalkylene compound and the nature of the alcohol or glycol used but it may be readily discovered because addition of slightly more than this amount of alcohol or glycol will cause a small separate layer of the alcohol to separate. The reaction mixture is preferably stirred during the addition of the alcohol and glycol and then left to stand for a period of time which will depend on the amount of reaction mixture being treated. Preferably the reaction mixture is allowed to stand for from 1 to 48 hours, at a temperature for example between 20° and 100° C., and then the solid material which has separated is removed. In the case of glycol the reaction mixture is allowed to stand at a slightly elevated temperature, for example, between 70° and 90° C. as this accelerates the separation of the solid material. The exact mechanism by which the alcohol or glycol used assists the separation of solid material is not at present fully understood but it is probable that the alcohol or glycol added increases the solubility of the inorganic salt in the reaction mixture and so enables larger crystals of this salt to form at the expense of the smaller by a "ripening" process over a period of time and these larger crystals may be easily separated from the reaction mixture. When the alcohol or glycol is not employed the solid material is probably present as a very fine suspension which cannot be removed either by filtration or centrifuging.

The solid material which separates after the treatment with alcohol or glycol consists largely of inorganic salts of the acid used in the previous step. This solid material separates in a crystalline form which is easily removed for example by sedimentation, filtration or

centrifuging or a combination of two or more of these methods. Filtration rates are high since the solid material is granular and not gelatinous and so can be filtered rapidly.

The alcohol or glycol may then be removed for example by distillation under reduced pressure. The resultant polyoxalkylene compound prepared according to the present invention has a low ash content for example the ash content is generally below 0.01% by weight.

In the preparation of polyoxalkylene compounds the product is generally contaminated with a small amount of unreacted alkylene oxide and although of course this will not affect the ash content, it will affect other properties of the final product, for example the flash point, and it is generally desirable to remove it. This can be done quite simply by heating the reaction mixture for example to a temperature about 90° C. preferably under reduced pressure for example about 10 to 50 mm Hg and preferably in an inert atmosphere for example an atmosphere of nitrogen. The time taken to remove the alkylene oxide will of course depend upon the scale of the preparation but usually heating as described above for period of approximately 30 minutes will suffice on the laboratory scale especially if the reaction mixture is continually agitated during this period. It is usual to carry out this process after the reaction mixture has been treated with acid and in the process of the present invention this procedure may if desired be followed but it is preferred to carry out this de-gassing operation, as it is known, before the reaction mixture has been treated with the acid.

The precise reaction conditions employed during the reaction between the alkylene oxide or alkylene oxides and starting material in the presence of an alkaline catalyst may be varied within fairly wide limits. However it is usual to conduct the reaction under increased pressure, preferably at a pressure between 20 and 60 psig, and more preferably between 30 and 40 psig. The pressure in the reaction chamber may be controlled by controlling the rate of addition of alkylene oxide. It is also usual to maintain the reaction mixture at an elevated temperature preferably between 100° and 125° C. The temperature of the reaction should preferably not exceed 130° C. since in many cases some decomposition occurs above this temperature.

A single alkylene oxide, for example ethylene oxide or 1:2-propylene oxide may be used in the reaction and the reaction conditions and amounts of reactants may be varied to give polyoxalkylene compounds of any desired molecular weight. The properties of the polyoxalkylene compounds may be varied by using a different starting material, for example if an alcohol is used the final product will be a monoether of a glycol whereas if a glycol is used as starting material a polyoxalkylene glycol will be formed.

However the properties of the polyoxalkylene compounds formed may be most readily varied by using two or more different alkylene oxides. For example polyoxalkylene compounds containing a high proportion of ethylene oxide tend to be water soluble whereas polyoxalkylene compounds containing a high proportion of a higher alkylene oxide, for example 1:2-propylene oxide tend to be insoluble in water. Thus many of the properties of the final product, for example its water solubility may be varied by using varying proportions of the different alkylene oxides employed. This may be done by mixing the alkylene oxides in the desired proportions before feeding this alkylene oxide mixture into the reaction vessel, in this way the various alkylene oxide units should be randomly distributed throughout the chain of the polyalkylene compound. This process has the advantage of being simple and reasonable control over the constitution final product is obtained. However it suffers from the disadvantage that the two different alkylene oxides will not react at the same rate, for example, higher molecular weight alkylene oxides react more slowly than lower molecular weight alkylene oxide, and this will lead to a preponderance of lower alkylene oxide units in the part of the polyoxalkylene compound which is formed first. Moreover any unreacted alkylene oxide left at the end of the reaction will tend to be predominantly the higher molecular weight alkylene oxide and this will lead to increased difficulties in de-gassing the polyoxalkylene compound, i.e., removing unreacted alkylene oxide.

Another way of varying the properties of the polyoxalkylene compound is to use as starting material a previously prepared polyoxalkylene glycol or monoether of such a compound and then react this compound with an alkylene oxide different from the one used to prepare the starting material. For example if a higher polypropylene glycol, which would be water insoluble, is used as starting material and reacted with ethylene oxide the polyoxalkylene compound formed has increased water solubility, the extent of this increase in water solubility depending upon the amount of ethylene oxide reacted.

However the method which it is preferred to employ in the preparation of polyoxalkylene compounds is that of block copolymerisation. This method has the advantage that a much closer control is obtained over the final constitution of the product, i.e. the proportion of various alkylene oxide units reacting and their positioning in the molecule of the polyoxalkylene compound. Moreover it may easily be arranged that the last alkylene oxide to be reacted is the alkylene oxide with the lowest boiling point and this procedure facilitates the degassing of the final product. This block copolymerisation method comprises condensing

an organic compound containing at least one hydroxyl, mercapto or amino group in the presence of an alkaline catalyst, with one or more equivalents of an alkylene oxide, subsequently with one or more equivalents of an alkylene oxide different from the first alkylene oxide, and then with one or more equivalents of an alkylene oxide different from the second alkylene oxide.

If desired one or more further condensations may be carried out, in each condensation one or more equivalents of an alkylene oxide, which is different from the one used in the previous condensation, being used.

In this process the alkylene oxides are added in blocks, the size of which may readily be controlled. Preferably constant amounts of two different alkylene oxides are condensed alternately. The relative amounts of the two different alkylene oxides used in each condensation stage may be varied thus varying the ratio of the two different alkylene oxide units in the final product. For example an alcohol such as butyl alcohol may be condensed with ethylene oxide and propylene oxide alternately, a fixed amount of ethylene oxide or a different fixed amount of propylene oxide being used in each condensation stage. Preferably those two fixed amounts of alkylene oxides reacting are such that condensation with one fixed amount of ethylene oxide followed by condensation with one fixed amount of propylene oxide increases the molecular weight of the product by about 400. The ratio of ethylene oxide to propylene oxide is preferably between 15:85 and 85:15. If the starting material already contains units of one of the alkylene oxides to be used, the first charge of that alkylene oxide is reduced by the corresponding amount. Thus for example if monobutyl ether of ethylene glycol is used as starting material and one of the alkylene oxides to be used is ethylene oxide, the first charge of ethylene oxide is reduced by the appropriate amount to compensate for the proportion of ethylene oxide units already present in the starting material.

The present invention is illustrated by the following Examples in which the term p.b.w. means parts by weight.

EXAMPLE I

A stainless steel reactor fitted with stirrer and heating coils was used for this preparation. A solution of 2.1 p.b.w. of potassium hydroxide in 41.6 p.b.w. of the monobutylether of ethylene glycol was placed in the reactor and the reactor purged with nitrogen. The reactor was closed and the contents heated to 110°C. Liquid ethylene oxide (6 p.b.w.) was then added to the reaction mixture and the ethylene oxide feed rate adjusted to maintain the pressure in the reactor at 50 to 60 psig. The temperature of the reaction mixture was never allowed to exceed 125°C. After the first charge of ethylene oxide had reacted propylene oxide (120 p.b.w.) was fed into the reaction mixture,

the feed rate being such that a pressure of 50 to 60 psig. was maintained and after this propylene oxide had reacted a further charge of ethylene oxide (22 p.b.w.) was added. Similar charges of propylene oxide and ethylene oxide to those described above were then added alternately, fresh charges not being added until the previous charge had substantially all reacted. This process was continued until the total amount of ethylene oxide added was 116 p.b.w. and the total amount of propylene oxide added was 720 p.b.w. When the final charge of propylene oxide had reacted the pressure was allowed to drop to 20 psig. before the reactor was cooled. The total reaction time was 13 hours 30 minutes. A portion of the reaction mixture (337 p.b.w.) was stripped by heating in a water bath under reduced pressure in the presence of nitrogen for 6 hours. The reaction mixture was treated with phosphoric acid to

neutralize the alkaline catalyst present and filtered. The residual polyoxyalkylene compound which now amounted to 321 p.b.w. was free from alkylene oxide and had an ash content of 0.29% by weight. The polyoxyalkylene fluid was then divided into several portions and homogenised with a different quantity of methanol by stirring the mixture for a short time. In some cases small quantities of water were also added to the mixture. After standing for about half an hour a precipitate appeared in the solution and gradually settled to the bottom of the vessel. The mixtures were then allowed to stand in the atmosphere for varying periods of time and then filtered to remove the inorganic material. Finally the methanol and water if present were removed by distillation under nitrogen. The results obtained are shown in Table I.

TABLE I

Amount of polyoxy-alkylene compound treated	Amount of methanol used	Amount of water added	Time of standing	Ash content of methanol treated product
2700 g	1000 g	—	2 days	0.03% w
1000 g	100 g	—	3 days	0.01 „
1000 g	1000 g	—	3 days	0.03 „
1000 g	2000 g	—	3 days	0.03 „
1000 g	100 g	—	2 days	0.01 „
82 kg	9.1 kg	—	1 day	0.035 „
305.5 kg	33.4 kg	—	1 day	0.02 „
2000 g	200 g	—	5 weeks	0.005 „
180 g	20 g	—	1 day	0.035 „
180 g	20 g	1 g	1 day	0.01 „
180 g	20 g	5 g	1 day	0.035 „
150 g	50 g	—	1 day	0.025 „
150 g	50 g	2.5 g	1 day	0.03 „
150 g	50	12.5 g	1 day	0.04 „

These results show that the methanol even if used in a proportion of 20% by weight based on the amount of polyoxyalkylene compound treated does reduce the ash content of the product but that 10% by weight of methanol gives better results.

EXAMPLE II

Samples of the polyoxyalkylene compound prepared as described in Example I were treated with varying quantities of different alcohols and glycols. The polyoxyalkylene compound was homogenised with the solvent by

stirring the mixture for a short time and the solution was allowed to stand in an open vessel for varying periods of time and was then filtered to remove the precipitated inorganic

material. The solvent was removed by distillation under nitrogen and the ash content of the product determined. The results obtained are shown in Table II.

TABLE II

Solvent	Ratio (by weight) of polyoxyalkylene compound to solvent	Time of standing	Ash content of treated product % w.
Methanol	9:1	2 days	0.01
Methanol	1:1	2 days	0.10
Industrial methlated spirits	9:1	2 days	0.09
Industrial methyiated spirits	1:1	2 days	0.03
Isopropanol	1:1	2 days	0.03
Normal propanol	1:1	2 days	0.02
Secondary butanol	1:1	2 days	0.06
Ethylene glycol	9:1	2 days	0.02 (after re-filtration)
Ethylene glycol	9:1	1 day (at 80° C.)	0.03

- 10 These results show that although other lower aliphatic alcohols and glycols can be used in this process methanol is to be preferred.

WHAT WE CLAIM IS:—

1. A process for preparing polyoxyalkylene compounds which comprises condensing an organic compound having at least one hydroxyl, carboxyl, mercapto or primary or secondary amino group with one or more alkylene oxides in the presence of an alkaline catalyst, treating with an acid to neutralize the alkali catalyst and subsequently treating with a lower aliphatic alcohol or glycol and removing the suspended solid material and the alcohol or glycol from the polyoxyalkylene compound.
2. A process as claimed in claim 1 in which the acid is an inorganic acid.
3. A process as claimed in claim 2 in which the inorganic acid is sulphuric acid or phosphoric acid.
4. A process as claimed in any one of the preceding claims in which the lower aliphatic alcohol or glycol is an aliphatic alcohol containing not more than 4 carbon atoms per molecule.
5. A process as claimed in any one of the preceding claims in which the lower aliphatic alcohol is methanol.
6. A process as claimed in any one of the preceding claims in which the amount of lower aliphatic alcohol or glycol used is between 3%

and 100% by weight based on the weight of the polyoxyalkylene compound.

7. A process as claimed in any one of the preceding claims in which the amount of lower aliphatic alcohol or glycol used is between 8% and 30% by weight based on the weight of the polyoxyalkylene compound.

8. A process as claimed in any one of the preceding claims in which the reaction mixture after treatment with the lower aliphatic alcohol or glycol is allowed to stand for between 1 hour and 48 hours before removing the suspended solid material.

9. A process as claimed in any one of the preceding claims in which the reaction mixture after treatment with the lower aliphatic alcohol or glycol is allowed to stand for between 12 hours and 24 hours before removing the suspended solid material.

10. A process as claimed in any one of the preceding claims in which the reaction mixture after treatment with the lower aliphatic alcohol or glycol is allowed to stand at a temperature between 20° and 100°C. before removing the suspended solid materials.

11. A process as claimed in any one of the preceding claims in which organic compound having at least one hydroxyl, carboxyl, mercapto or amino group is a phenol, an alcohol, a glycol or the monoether of a glycol.

12. A process as claimed in claim 11 in

which the alcohol is an aliphatic alcohol.

13. A process as claimed in claims 11 and 12 in which the alcohol is n-butanol.

14. A process as claimed in claim 11 in which the monoether of a glycol is the mono-butyl ether of diethylene glycol.

15. A process as claimed in any one of the preceding claims in which the condensation is carried out at a pressure of between 20 psig. and 60 psig. and a temperature of between 100° C. and 125° C.

16. A process as claimed in any one of the preceding claims in which the alkylene oxide or two or more alkylene oxides are selected from ethylene oxide, 1:2-propylene oxide and 1:2-butylene oxide.

17. A process as claimed in any one of the preceding claims in which the alkylene oxide or two or more alkylene oxides contain not more than 0.1% of aldehyde and not more than 0.1% of water.

18. A process as claimed in any one of the preceding claims in which a mixture of two or more alkylene oxides is employed.

19. A process as claimed in claim 18 in which the mixture of alkylene oxides is a mixture of ethylene oxide and propylene oxide in the ratio of from 1:10 to 10:1.

20. A process as claimed in any one of claims 1 to 19 in which the organic compound containing at least one hydroxyl, carboxylic, mercapto or amino group is condensed, in the presence of an alkaline catalyst, with one or more equivalents of an alkylene oxide, sub-

sequently with one or more equivalents of an alkylene oxide different from the first alkylene oxide, and then reacted with one or more equivalents of an alkylene oxide different from the second alkylene oxide.

21. A process as claimed in claim 16 in which one or more further condensations are carried out, in each condensation one or more equivalents of an alkylene oxide, which is different from the one used in the previous condensation one or more equivalents of an alkylene oxide, which is different from the one used in the previous condensation, being reacted.

22. A process as claimed in any one of the preceding claims which comprises removing unreacted alkylene oxide prior to treating the reaction mixture with acid.

23. A process as claimed in any one of claims 1 to 21 which comprises removing unreacted alkylene oxide after treatment of the reaction mixture with acid.

24. A process for preparing polyoxyalkylene compounds as hereinbefore described with particular reference to the Examples.

25. A polyoxyalkylene compound prepared by a process as claimed in any one of the preceding claims.

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